A CONDUCTOMETRIC STUDY OF THE INFLUENCE OF CONCENTRATION AND TEMPERATURE ON THE REACTION VELOCITY OF 2,4-DINITRO-CHLOROBENZENE WITH PIPERIDINE IN 95 PER CENT ETHANOL

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by

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CHAPTER I

INTRODUCTION

Determination of reaction rates has been accomplished by various means which utilize either chemical or physical properties of the reaction components. The main function of both methods is to ascertain what portion of the reaction has taken place after a specified time.

The use of a chemical property implies a direct determination of the concentration of the reagents or products by standard quantitative methods--volumetric or gravimetric analysis. Important restrictions of the two methods are the need to: (1) make standard solutions, (2) remove an aliquot of the reacting solution, (3) quench the reactions, and (4) derive conclusions on a few discontinuous readings.

The more convenient is the physical method. Frost and Pearson[1] describes a physical method as one in which some physical property of the reaction mixture, which changes as the reaction proceeds, is measured. It is necessary for the physical property to change linearly with the concentrations of the reactants and products. Common among physical methods are pressure measurements in gaseous reactions; dilatometry,

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[1]Arthur Frost and Ralph Pearson, Kinetics and Mechanism (New York: John Wiley and Sons, 1962), p. 27.

or measurement of volume change; optical methods such as polarimetry, refractometry, colorimetry, and spectrophotometry; and electrical methods such as polarography, potentiometry, and conductivity.[1] Many chemical reactions which proceed with the formation or disappearance of ions, or changes in the nature of the ions, are feasible for conductometric studies.[2]

The reaction between 2,4-dinitrochlorobenzene and piperidine in 95 per cent ethanol proceeds with the formation of 2,4-dinitrophenylpiperidine, piperidinium ions, and chloride ions.

$$C_6H_3(NO_2)_2Cl + 2C_5H_{11}N \rightarrow C_6H_4(NO_2)_2C_5H_{10}N + C_5H_{12}N^+ + Cl^-$$

All reaction kinetics of this reaction have been obtained by methods which necessitated the removal and quenching of aliquots of the reacting solution. It would be of interest and value to study the reaction kinetics of 2,4-dinitrochlorobenzene with piperidine by a method which would allow the progress of the reaction to be followed continuously and at the temperature at which the reaction was taking place.

The problem, then, was to determine conductometrically the reaction velocity and the Arrhenius parameters for the reaction between 2,4-dinitrochlorobenzene and piperidine in 95 per cent ethanol for various concentrations and temperatures.

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[1] Ibid., p. 28.

[2] Duncan MacInnes, The Principles of Electrochemistry (New York: Reinhold Publishing Corporation, 1950), p. 378.

CHAPTER II

REVIEW OF THE LITERATURE

Electricity has been used to study chemical phenomena since Carlisle and Nicholson decomposed water by electrolysis in 1800.[1] The alternate decomposition and recombination of atoms, with the liberation of a gas at each electrode, occurred when a current was passed through an electrolyte. Baron C. J. von Grotthuss proposed the preceding explanation to account for electrical conductance of certain solutions.[2] According to Grotthuss' theory, the electrically charged particles only existed when a current was passed. In 1857, Rudolph Clausius theorized the existence of electrically charged particles (ions) caused by energetic collisions of undisassociated molecules in electrolyte solutions. These particles were guided by an applied E.m.f. but were not the products of it.[3] From his studies of electrolytes, Clausius found that an electrical current through an electrolyte was

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[1] Ibid., p. 20.

[2] Ibid.

[3] Walter Moore, Physical Chemistry (New York: Prentice-Hall, Inc., 1955), p. 437.

governed by Ohm's Law.[1] G. Quincke[2] verified Clausius' findings and found no exceptions. Svante Arrhenius' theory that salts in aqueous solutions are largely disassociated into free ions led support to Clausius' theory.[3]

In 1876, Fredrick Kohlrausch perfected a precise technique, as described in Des Leitvermogen der Electrolyte, for determining a solution's conductance. Using an alternating current with a Wheatstone bridge, invented by Charles Wheatstone in 1843 and modified by the addition of a slidewire by Kirchoff[4], Kohlrausch accurately measured the resistance (or conductance) of an electrolyte. One arm of the bridge was a cell containing the solution of unknown resistance, another arm was a resistance decade box of sufficient range to allow an approximate resistance of the cell to be achieved, and the final two arms of the bridge were composed of a divided slidewire of uniform cross sectional area. A null-point was detected by the use of head

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[1]H. R. Raikes, "Ions and the Conductance of Electricity," Transaction of the South African Institute of Electrical Engineers, XXVII (June, 1936), 149.

[2]G. Quincke, "On Electrolysis and Conductance of Electricity Through Liquids," Journal of the Chemical Society, XXV (1872), 207.

[3]MacInnes, loc. cit.

[4]Florian Cajori, History of Physics (New York: The MacMillan Company, 1917), p. 232.

phones. Kohlrausch minimized the polarization of shiny platinum electrodes by electroplating finely divided platinum upon them from a chloroplatinic solution to which a small trace of lead acetate had been added.[1] Jones and Bollinger[2], in 1935, found that a thin velvety black coating of platinum was sufficient to minimize polarization when a frequency of 1000 to 5000 cycles per second was used. These authors found that the lowering of the actual cell resistance from the true cell resistance due to the capacitative shunt between parts of the cell of opposite polarity could be eliminated by proper cell design.[3] Hovorka and Mendenhall[4] and Buck and Smith[5] used cathode-ray tubes to detect the balance of the bridge and found no loss of sensitivity in comparison with earphones.

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[1]Grinnell Jones and Dorothy Bollinger, "The Measurement of the Conductance of Electrolytes. VII. On Platinization," Journal of the American Chemical Society, LVII (1935), 280.

[2]Ibid.

[3]Grinnell Jones and Dorothy Bollinger, "The Measurement of the Conductance of Electrolytes. III. Design of Cells," Journal of the Chemical Society, LIII (1931), 411.

[4]Frank Hovorka and Elwyn Mendenhall, "A Cathode-Ray Tube Alternating Current Bridge Detector for Conductivity Measurements," Journal of Chemical Education, XVI (1939), 239.

[5]Kenneth Buck and Gilbert Smith, "Null-Point Detector for Direct and Alternating Current and its use in Conductance and E.m.f. Measurements," Transactions of the Faraday Society, XXXXI (1945), 588.

In 1888, Negreano[1] determined the progress of an etherification by conductivity measurements. Price[2] and McIlhiney[3] followed the reaction of ethyl alcohol and hydrochloric acid. Rivett and Sidgwick[4] in 1910 and Grunberg[5] in 1962 determined conductometrically the reaction rate of the formation of acetic acid from the anhydride in water. Cody and Lictenwalter[6] were the first to study reaction rate by conductivity methods in non-aqueous solutions. Since then many reactions have been studied conductometrically: (1) benzyl chloride in formic acid[7], (2) alkyl halides with po-

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[1]Negreano, "Velocity of Etherification Determined by Means of Electrical Conductance," Journal of the Chemical Society, LIV (1888), 1025.

[2]Thomas Slater Price, "The Reaction of Ethyl Alcohol and Hydrochloric Acid," Journal of the Chemical Society, LXXIX (1901), 303.

[3]Parker C. McIlhiney, "A Method for Determining the Resistances of Electrolytes," Journal of the American Chemical Society, XX (1898) 206.

[4]Albert Rivett and Nevil Sedgwick, "The Rate of Hydration of Acetic Anhydride," Journal of the Chemical Society, LXXXXVII (1910), 732.

[5]David B. Greenberg, "Reaction Kinetics from Conductivity Data," Journal of the Chemical Education, XXXIX (1962), 140.

[6]H. P. Cody & H. O. Lictenwalter, "Chemical Reactions and Electrical Conductivity of Non-aqueous Solutions," Journal of the American Chemical Society, XXXV (1913), 1434.

[7]Alwyn G. Evans and S. D. Hamann, "Energy and Entropy Changes of Organic Reactions," Transactions of the Faraday Society, XXXXVII (1951), 26.

tassium iodide in acetone[1], (3) alkyl halides with tertiary amines, and (4) solvolysis of tertiary butyl chloride.[2] Of the numerous reaction studies cited, only Chesick and Patterson and Greenberg related the reaction kinetics in terms of resistances and no studies had the reaction kinetics in terms of conductances.

The first quantitative kinetics measurement was made by Ludwig Wilhelmy in 1850. He measured the inversion of cane sugar in aqueous solutions of acids with time.[3] Wilhelmy found that the rate of decrease of sugar at any instant was proportional to the concentration of unconverted sucrose remaining. Berthlote and St. Gillis, in 1862, found similar results with their equilibrium studies between ethanol, acetic acid, ethyl acetate, and water.[4] In 1867, Harcourt and Esson published results of an investigation concerning the reaction of potassium permanganate with oxalic acid and hydrogen peroxide with iodic acid.[5] They calculated the

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[1]Brynmar Jones and D. J. Worsfold, "Determination of Reaction Rates by Conductivity Measurements," Nature, CLXVII (1951), 1072.

[2]John Chesick and A. Patterson, Jr., "Determination of Reaction Rates with an A. C. Conductivity Bridge," Journal of Chemical Education, XXXVII (1960), 242.

[3]Moore, op. cit., p. 528.

[4]Keith J. Laidler, Chemical Kinetics (New York: McGraw-Hill Book Company, Inc., 1950), p. 1.

[5]A. Vernon Harcourt and W. Esson, "On the Observations of the Course of Chemical Change," Journal of the Chemical Society, XX (1867), 461.

second order rate constant similarly to present methods.

Calhours[1] first synthesized piperidine in 1854 by the distillation of piperine with potash lime. He found that piperidine dissolved in water and was a colorless base with a formula of $C_5H_{11}N$. In 1933, Opstall[2] studied 2,4-dinitrochlorobenzene with piperidine in absolute alcohol at zero degrees centigrade and twenty-five degrees centigrade. He determined the chloride ion concentration by titrating with silver nitrate and found the reaction to be of the second order. Blanksma and Scrinemaker studied the reaction of primary and secondary amines on 2,4-dinitrochlorobenzene in absolute alcohol by the disappearance of the amine.[3] Brady and Cropper[4] studied the same reaction but determined the progress of the reaction by the volumetric analysis of the chloride. They verified the reaction being of the second order and determined that the dinitrophenylpiperidine produced did not react with the 2,4-dinitrochlorobenzene nor was

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[1]A. Cahours, "On Piperidine, A New Alkali Derived from Piperine," The Quarterly Journal of the Chemical Society, VI (1854), 175.

[2]H. J. Opstall, "Reaction Velocity of 1-chloro-2,4-dioltrobenzene and 1-chloro-2,4-dinitronaphthalene with Aromatic Amines," Recueil des travaux chimiques des Pays-Bas, LIII (1933), 901-911; Chemical Abstract, Volume 28 (1934), 26.

[3]O. L. Brady and F. R. Cropper, "The Reaction Between Amines and 1-chloro-2,4-dinitrobenzene," Journal of the Chemical Society, LXXII (1950), 507.

[4]Ibid.

the alcoholysis appreciable. Bunnett and Davis[1] determined t
the reaction kinetics of 2,4-dinitrochlorobenzene with piperidine in sixty per cent dioxane. Bunnett, Gabisch, and Pruitt[2] studied the Arrhenius parameters of 2,4-dinitrochlorobenzene with piperidine in 95 per cent ethanol at twenty-five degrees centigrade and zero degrees centigrade. They determined that the formation of an unstable intermediate substance was the most probable rate determining mechanism.

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[1] J. F. Bunnett and G. Davis, "Kinetics of Reaction of 2,4-dinitrochlorobenzene with Some Familiar Nucleophilic Reagents," Journal of the American Chemical Society, LXXVI (1954), 3011.

[2] J. F. Bunnett, Edgar W. Garbisch, Jr., and Kenneth M. Pruitt, "The 'Element Effect' as a Criterion of Mechanism in Activated Aromatic Nucleophilic Substitution Reactions," Journal of the American Chemical Society, LXXIX (1957), 385.

CHAPTER III

METHODOLOGY AND CALCULATION

I. METHODOLOGY

The problem was to measure the resistances (R_t) of the reacting solutions after known times had elapsed from the start of the reactions. The concentrations of the reagents and the reaction temperatures were varied to ascertain their influence upon the Arrhenius parameters determined conductometrically.

The Wheatstone bridge circuit used to measure the resistances is shown in Figure 1. Either Cell A or Cell B, depending on which cell resistance was being determined, constituted one arm of the bridge. Cells A or B could be placed alternately in the circuit by means of the double pole double throw switch, G. Two General Radio decade boxes of the 1432-Q and 1432-P series gave a range of one-tenth ohm to one megohm resistance. The accuracy of the coils was .05 per cent for the coils equal to or greater than one hundred ohms.[1] For the coils below one hundred ohms the accuracy was 0.1 per cent. These decade boxes allowed coarse approximations of the resistances in the conductivity cells to be achieved

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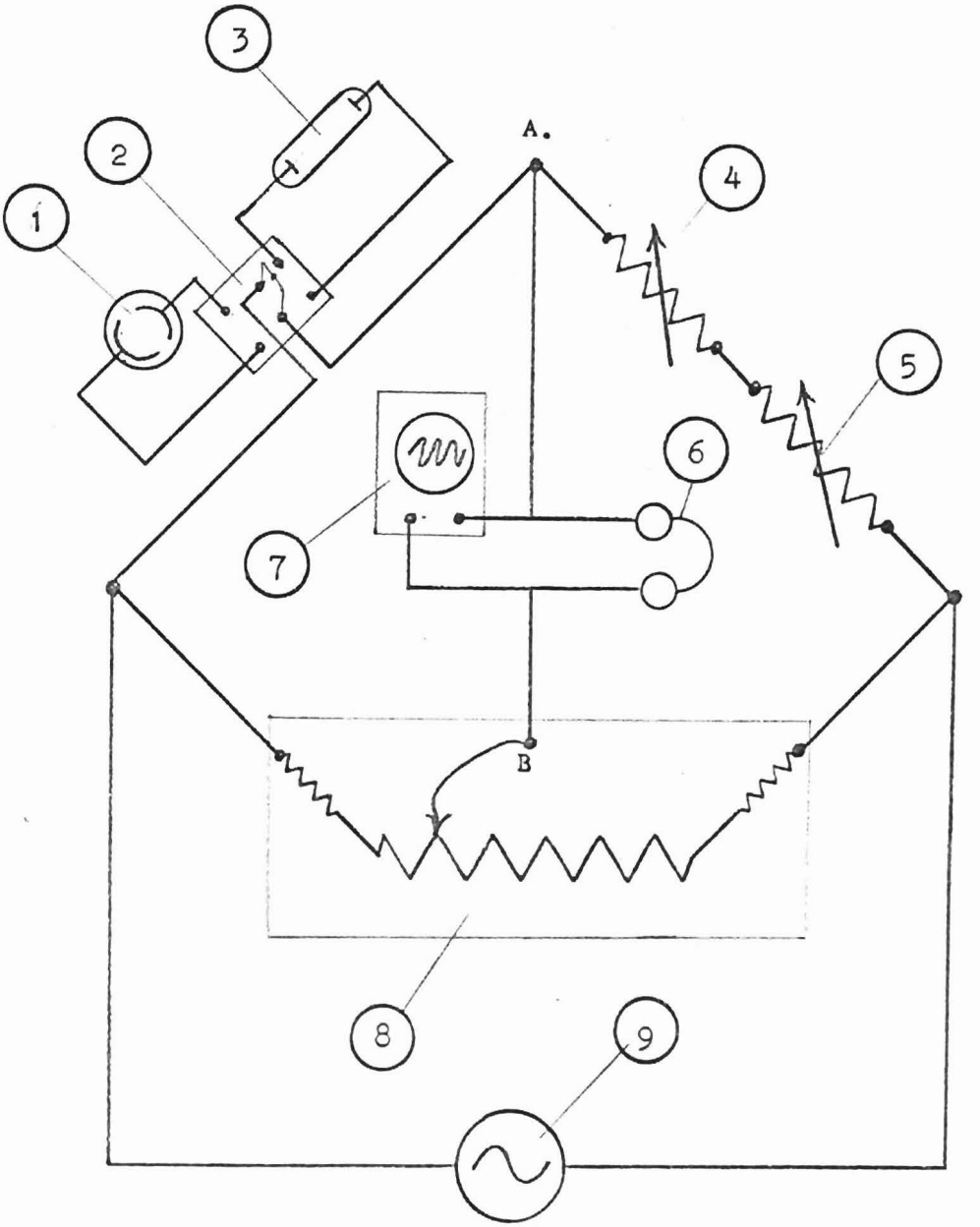
[1]General Radio Company, Catalog, No. R, (West Concord, Massachusetts: General Radio Company, 1963), 161.



1. Conductivity cell A
2. Double-pole, double-throw switch
3. Conductivity cell B
4. General Radio decade resistor, type 1432-P
5. General Radio decade resistor, type 1432-Q
6. Headphones
7. Oscilloscope
8. Leeds & Northrup slide wire
9. Signal generator

and comprised the second arm. A student Kohlrausch slidewire, manufactured by Leeds and Northrup Company, was used to obtain the final balance between the decade boxes and the conductivity cell. The center tap thus separated the third and fourth arms. The student slidewire consisted of a slidewire of approximately thirty-five centimeters in length calibrated into two hundred units and two end coils (550 ohms) each four and one-half times the resistance of the wire (122 ohms). This allowed the slidewire to be one-tenth of the complete circuit.[1] The slidewire was calculated by $\frac{4500 + A}{5500 - A}$ where A was the dial reading. The two ratio extremes are 0.8182 and 1.2217 when A equalled 1 and 999 dial units respectively. All resistances were determined using the end coils of the slidewire to insure the greatest accuracy.

When the points A and B were at the same potential, a null-point was achieved. The null-point was determined by the absence or minimum of sound on the head phones and the formation of a straight horizontal line on a Model 670 Hickok oscilloscope screen. It was found that the oscilloscope allowed a quicker, more definite null-point detection for high resistances at the beginning of a reaction. The head phones were more sensitive at the end of the reaction when the resistances were lower and not changing rapidly.

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[1]Eimer and Amend and Fisher Scientific Company, Modern Laboratory Appliances, No. 90, (New York: Fisher Scientific Company, Ltd., 1942), p. 425.

A variable capacitor in parallel with the electrolyte cells did not effect the "sharpness" of the null-point. By using shielded wires, interfering magnetic fields were minimized. The shielded wires were grounded to the building water system. Without shielding, definite null-points were unattainable.

Since an audio, as well as a visual, determination of the bridge balance was desired, a one-thousand cycle audio frequency oscillator with a pure sine wave and free from harmonics was used. A preparatory study was made using a variable frequency oscillator to determine the effect of frequency upon the null-point. No noticeable change was observed.

The timing devices used in this study were a Nuclear Chicago Model T-101 timer which measured to the nearest hundredth of a minute and an ordinary General Electric wall clock with a sweep second hand. The Model T-101 was started manually by a pressure switch on the floor upon the introduction of piperidine into the conductivity cell already containing the proper amount of 2,4-dinitrochlorobenzene. After the reaction proceeded sufficiently to minimize the importance of the time factor, the timing was transferred to the wall clock.

In order to have as nearly constant temperature as

possible for the reaction, a large water bath was used. The entire bath was insulated with one-half inch thick spun glass. The temperature of the water was measured with a one-tenth degree centigrade interval thermometer. For approximately zero degrees centigrade, a sufficient amount of ice cubes were kept in the bath and the ice-ice water mixture was constantly stirred by an electric stirrer. At twenty-five degrees and forty degrees, a seven hundred and fifty watt heater coil was used to introduce heat into the system while another coil, attached to the cold water tap, was used to quickly cool the system or to act as a balance against the heating coil.

The thermostats were of the vapor type. The liquids used in the thermostats were ethyl ether for twenty-five degrees and carbon disulfide for forty degrees. The thermostats were connected to a relay which in turn controlled the heating coil. A Fisher catalog indicated a thermostat of this type capable of accuracy within a range of four one-hundredths of one degree.[1] Care was taken to submerge the thermostat the same depth as the conductivity cells and thermometer. This was approximately three centimeters from the surface.

The Kohlrausch type conductivity cells were used. Cell A was designed for measuring electrolytes with large

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[1] Ibid., 906.

resistances because of large electrode surface area and the closeness of the two electrodes. Cell B was constructed for electrolytes with solution resistances less than those for Cell A.

Since polarization of the shiny platinum electrodes could give erroneous resistances, a thin velvety black platinum coating was electroplated on the electrodes from a chloroplatinic acid solution (H_2PtCl_6) to which a trace (.02 grams) of lead acetate had been added. Bollinger and Jones[1] found the platinum black flaked-off when the trace of lead acetate was omitted. The electroplating of the platinum from the solution was accomplished by regulating the current from a three volt dry cell with a forty-four ohm rheostat, before it entered the conductivity cell. The current was reduced until only a few bubbles were being liberated at the electrode. The direction of the current was reversed approximately every thirty seconds until a velvety black coating remained on both electrodes. This procedure took place rapidly in Cell A but Cell B required at least eight minutes, depending upon the strength of the current. The cells were then filled and emptied six times each with six normal sulfuric acid. After filling the cells

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[1]Grinnell Jones and Dorothy M. Bollinger, "The Measurement of the Conductance of Electrolytes. VII. On Platinization," Journal of the American Chemical Society, LVII (1935), 283.

the seventh time with the acid, a much stronger current, which was reversed every minute for thirty minutes, was allowed to pass through cells in order to remove any gases (chlorine) occluded from the preceding process. The cells were then rinsed with distilled water four times and allowed to remain at room temperature for at least four hours.

Conductivity water for determining the cell constants was prepared by re-distilling distilled water in an all glass system, and collecting the water hot to prevent carbon dioxide from re-dissolving. A polyethylene vessel was used to store the conductivity water in order that no ions would be dissolved from the vessel.

The cell constants of cells A and B are dependent upon the geometrical configuration of the electrodes and thereby should indicate any inherent changes in the cells at the commencement and termination of this study. The determination of the cell constants also allowed a check of the reproducibility of system. By finding the resistances of known concentrations of potassium chloride solutions whose specific conductances are known, the cell constant can be determined using

$$K = LR$$

with K being the cell constant, L the specific conductance, and R the resistance of a potassium chloride solution. The specific resistance of a conductor is defined as the resistance

in ohms of a solution between two electrodes one centimeter apart and with a one square centimeter cross-section.[1] The specific conductance is the reciprocal of the specific resistance. The concentrations and their respective specific conductances at twenty-five degrees centigrade are given in Table I.

TABLE I[2]

THE SPECIFIC CONDUCTANCES OF VARIOUS CONCENTRATIONS OF POTASSIUM CHLORIDE AT 25° C.

Concentration of Potassium Chloride in moles liter^{-1}	Specific Conductance in mhos cm^{-1}
.001	.0001469
.005	.0007175
.01	.001413

The potassium chloride solutions were prepared ten times the desired strengths. Potassium chloride which assayed at 100.0 per cent was used. Fifty milliliter aliquots of the solution were removed and diluted in a volumetric flask to five hundred milliliters with conductivity water. The solutions were stored in polyethylene bottles. The conduc-

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[1]H. Jermain Creighton, Principles and Applications of Electrochemistry (London: Chapman and Hall Company, 1935), p. 574.

[2]Grinnell Jones and Benjamin Bradshaw, "The Measurement of the Conductance of Electrolytes. V. Strong Electrolytes," Journal of the American Chemical Society, LV (1933), 1780.

tivity cells, after being rinsed several times with the potassium chloride solutions, were filled and placed in the twenty-five degree water bath until thermal equilibrium was attained. Resistances of the cells were measured using three different settings on the decade boxes. To insure against erroneous results due to the solution concentration, at least three different solutions were prepared at each concentration. The potassium chloride crystals were weighed to the nearest one-tenth of a milligram.

After the cell constants were determined and the apparatus' reliability proven acceptable, the solutions for determining the reaction kinetics of 2,4-dinitrochlorobenzene with piperidine in 95 per cent ethanol were prepared. The piperidine solution was prepared so that ten milliliters contained the desired number of moles of piperidine to be introduced into the cells. Two solutions of 2,4-dinitrochlorobenzene were prepared so that 18.5 milliliters for cell A and 29.0 milliliters for cell B contained the desired number of moles. The concentrations of 2,4-dinitrochlorobenzene chosen for this reaction study were ,001 moles, .002 moles, and .0025 moles in 18.5 and 29.0 milliliters of prepared solutions. The concentrations in moles of the piperidine in 10 milliliters of solution were twice the 2,4-dinitrochlorobenzene. For cell A the actual concentrations of the 2,4-dinitrochlorobenzene in moles per liter involved

in the reactions are .0351, .0702 and, .0887 for the corresponding concentrations .0010, .0020 and, .0025 moles per 18.5 milliliters of solution. For cell B, the corresponding initial concentrations of 2,4-dinitrochlorobenzene in moles per liter are .0256, .0513 and, .0641 for .0010, .0020 and, .0025 moles respectively. The concentrations of 2,4-dinitrochlorobenzene and piperidine were such that there were two molecules of piperidine for every one molecule of 2,4-dinitrochlorobenzene.

These concentrations were chosen because the resistances taken during the reaction could be easily measured. The solid reagent was placed into a volumetric flask approximately three-fourths filled with 95 per cent ethanol and dissolved. It was found that the rate of solution of the 2,4-dinitrochlorobenzene in 95 per cent alcohol could be increased by placing the volumetric flask into water at approximately fifty degrees and by occasionally shaking the flask. The piperidine was measured into a 100 ml volumetric flask with a five milliliter pipet graduated in one-tenths of one milliliter. The solutions were then diluted to mark.

The resistances of the reacting solution were first determined when the reaction occurred at twenty-five degrees centigrade. The procedure was as follows:

1. Prepare solutions as described previously.
2. Introduce the proper volume (18.5 ml and 29 ml for cell A and cell B respectively) of 2,4-dinitrochlorobenzene by means of a 50 ml buret.
3. Place the cells in the water bath and allow the 2,4-dinitrochlorobenzene to come to temperature.
4. Place the volumetric flask containing the piperidine solution in the water bath and allow it to reach thermal equilibrium.
5. Pipet 10 ml of piperidine into cell A and cell B. Start the timer when approximately one-half of the solution is in the cell.
6. Measure the time for the first few null-points to be reached at a preset reading of 500 on the slidewire and preset resistances on the decade box.
7. Measure the resistances of the cell for specific known times after the reaction has started and until a constant resistance is obtained.

At forty degrees the pipet method for introducing the piperidine into the cells was inaccurate. A ten milliliter hypodermic syringe, suggested by Doctor F. E. Jacob, proved to be ideal. The syringe, with a piece of plastic

tubing placed over the needle after being filled with piperidine, was placed in the water bath and allowed to come to temperature. The syringe was wiped with an absorbent cloth after being removed from the water bath to prevent the introduction of water into the system. The needle was placed into the solution of 2,4-dinitrochlorobenzene to allow the force of the entering piperidine to thoroughly mix the two reactants. The same procedure was followed at 0.2 degrees centigrade as at forty degrees.

II. CALCULATIONS

The reaction rate, or reaction velocity, is defined as the rate of change of concentration of a substance involved in a reaction at a fixed temperature.[1] Since the rate almost invariably changes with time, a derivative, dCa/dt is used to express the relationship; C_a is the concentration of a reactant. The use of concentration in defining a reaction rate makes the rate an intensive property (i.e. independent of size). This dependence of the rate on concentration is shown through a proportionality factor, k, which is known as the specific reaction rate, rate constant, or rate coefficient. It is numerically

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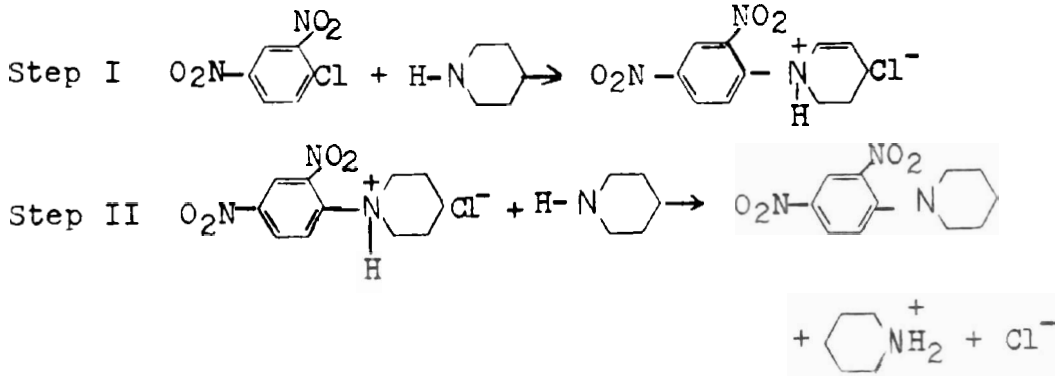
[1]Frost and Pearson, op. cit., p. 9.

equal to the reaction rate when the reactants are present in unit concentration and it has the dimensions of

$$k = (\text{concentration})^{n-1}\ (\text{time})^{-1}$$

where n is the order of the reaction. Glasstone and Lewis defines the order of the reaction as "the number of atoms or molecules whose concentrations determine the rate of the reaction".[1]

A second order reaction rate is proportional to the first power of the concentration of two reactants or to the second power of one substance's concentration. Bunnett and Crockford[2] and other experimenters found the reaction between 2,4-dinitrochlorobenzene and piperidine to be of second order in 95 per cent ethanol as well as absolute ethanol. This reaction proceeds in two steps with the first being the slow or rate determining step.



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[1] Samuel Glasstone and David Lewis, Elements of Physical Chemistry (New York: D. Van Nostrand Company, Inc., 1960), p. 601.

[2] J. F. Bunnett and H. D. Crockford, "A Versatile Experiment in Reaction Kinetics for Physical Chemistry Laboratory," Journal of Chemical Education, XXXII (1956), 556.

The reaction rate for this reaction would be

$$\frac{dx}{dt} = k(a-x)(b-2x)$$

where x is the amount of either 2,4-dinitrophenylpiperidine or piperidinium chloride produced at time t, a is the original concentrations of 2,4-dinitrochlorobenzene, and b is the original concentration of piperidine. If the initial concentration of piperidine is made exactly twice the initial concentration of 2,4-dinitrochlorobenzene, the reaction rate expression is modified and becomes

$$\frac{dx}{dt} = k(a-x)(2a-2x)$$
$$= 2k(a-x)^2$$

Integrating the modified rate expression and calculating the constant of integration, one obtains

$$\frac{1}{(a-x)} = 2kt + \frac{1}{a}$$

Conductivity is a measure of the total ions and is not only dependent upon kinds of ions but also the concentrations of the various species. Equivalent conductance (Λ) is the conductance of a solution containing one gram equivalent per liter of solution and is expressed by

$$\Lambda = 1000 \frac{L}{c}$$

where L is the specific conductance and c is the concen-

tration of the solution in gram equivalents per liter. Solving the above expression for the specific conductance and substituting $\frac{Kcell}{R}$, the expression becomes

$$\frac{c\Lambda}{1000} = L = \frac{Kcell}{R}$$

or $$\frac{\Lambda c}{1000\ Kcell} = \frac{1}{R} = C$$

where C is the total conductance of the solution. By assuming Kohlrausch's law of independent migration of ions to be applicable (at infinite dilution, each ion makes a definite contribution toward the equivalent conductance of an electrolyte)[1], one obtains

$$C = \frac{1}{1000\ Kcell} \sum_{y} c_y\ l_y$$

where l = equivalent ionic conductances

c = concentrations of ionic species in equivalents per liter

Kcell = cell constant.

For the reactions being considered, the three conductances are

$$C_o = \frac{(2a l_{pip.})}{1000\ K}$$

$$C_t = \frac{(Xl_{chloride} + {}^{x}l_{piperidinium} + {}^{(2a-2x)}l_{pip.})}{1000\ K}$$

$$C_\infty = \frac{(a l_{chloride} + {}^{a}\ l_{piperidinium})}{1000\ K}$$

where C_o, C_t, and C_∞ are conductances at times o, t, and ∞ minutes respectively.

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[1] Glasstone and Lewis, op. cit., p. 441.

After subtracting C_o from both C_t and C_∞, the equivalent ionic conductances and the cell constant were eliminated by dividing the two differences.

$$\frac{C_t - C_o}{C_\infty - C_o} = \frac{x}{a}$$

Solving of the above expression for x and substituting into the integrated rate equation permitted the reaction rate to be expressed in terms of conductances, which are linear functions of the molar concentrations. The conductances were all calculated from the reciprocals of the resistances. The substituted rate equation becomes

$$\frac{C_\infty - C_o}{C_\infty - C_t} = 2kat + 1$$

which is in the point-slope equation of a straight line. Thus, a plot of $\frac{C_\infty - C_o}{C_\infty - C_t}$ versus t should give a straight line whose slope equals 2ka and that has a y-intercept of 1. The slopes and y-intercepts of the best lines through the plotted points were obtained from the method of least squares,[1]

$$\text{y-intercept} = \frac{\sum(x) \sum(xy) - \sum(x^2) \sum(y)}{\left[\sum(x)\right]^2 - n \sum(x^2)}$$

$$\text{slope} = 2ka = \frac{\sum(x) \sum(y) - n \sum(xy)}{\left[\sum(x)\right]^2 - n \sum(x^2)}$$

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[1] J. W. Mellor, Higher Mathematics for Students of Chemistry and Physics (New York: Dover Publications, Inc., 1955), p. 327.

where y = conductance ratio, $\frac{C_\infty - C_o}{C_\infty - C_t}$

x = time in minutes

n = number of plotted points.

The half-life, amount of time necessary for one-half the original concentration to react, was determined by substituting 1/2a for x into the integrated rate equation. The substituted equation becomes

$$\frac{1}{2ka} = t_{\frac{1}{2}}$$

which is $\frac{1}{\text{slope}}$.

The dependence of the specific rate constant on temperature was first presented by von't Hoff[1] in 1887 and extended in 1889 by Svante Arrhenius. Arrhenius thought a reasonable equation for the variation of the rate constant with temperature might be

$$\frac{d\ln k}{dT} = \frac{E}{RT^2}$$

which becomes upon integration

$$\ln k = -\frac{E}{RT} + \text{constant}$$

where the constant equals ln A. This is the famous Arrhenius equation, but it is usually written in the following exponential form:

$$k = Ae^{-E/RT}$$

---

[1]Laidler, op. cit., p. 57.

where A is the frequency factor with the dimensions of the specific rate constant, e^{-R}/RT is the Boltzmann factor, E the energy of activation in kilocalories, R the universal gas constant equal to 1.987 calories degree^{-1} mole^{-1}, and T is the absolute temperature in degrees Kelvin. Taking the common logarithm of the integrated form, one obtains

$$\log k = \log A - \frac{E}{2{,}303\ RT}$$

which should yield a straight line if log k versus 1/T is plotted. The line would have a slope equal to $\frac{-E}{2{,}303R}$ and a y-intercept of log A. The slope of the straight line obtained from figure 8 was $-2.313X10^{3}$, thus,

$$(2.303)(1.987)(-2.313X10^{3}) = -E$$

$$10.66 \text{ Kcal.} = E$$

The integral between limits of the Arrhenius expression yield

$$\log {}^{k2}/_{k1} = \frac{E}{2.303R}\left(\frac{T_2 - T_1}{T_2\ \ T_1}\right)$$

Taking two points on the line from figure 8, an activation energy, E, calculated from the slope gave a value of 10.58 Kcal.

If one supposes an equilibrium exists between reacting molecules and a very unstable intermediate which decomposes into the products of the reaction, it is possible to derive

an equation for the specific reaction rate of any reaction, namely

$$k = \frac{RT}{Nh} K^*,$$

where N is Avogardro's number, h is Planck's constant, and K* is the equilibrium constant between the reactants and the activated state. Thermodynamically, it can be shown that

$$K^* = e^{S^*/R} \; e^{-E/RT}$$

which after substitution becomes

$$k = \frac{RT}{Nh} \; e^{S^*/R} \; e^{-e/RT}$$

Taking the logarithm of the above expression one obtains

$$\log k = \frac{S^*}{2{,}303\ R} - \frac{E}{2.303RT} + \log \frac{RT}{Nh}$$

Using the values of 1.744 liters $mole^{-1}$ $second^{-1}$ and 298.3 degrees absolute for k and T respectively, one finds the change in entropy to be 21.84 calories.

TABLE II

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0010 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT 0.2° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\Sigma d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.40	12,000	0.03[a]	0.02	1.012
0.58	10,000	0.06[a]	0.02	1.018
0.89	8,000	0.05[a]	0.02	1.028
1.00	7,475	130.000	76.58	1.029
2.00	4,674	119.60	53.49	1.055
3.00	3,528	55.86	24.50	1.079
4.00	2,856	16.64	7.44	1.103
5.00	2,428	32.40	14.49	1.126
6.00	2,134	28.98	14.49	1.148
7.00	1,902	20.12	9.00	1.171
8.00	1,726	14.25	6.37	1.194
9.00	1,590	15.65	7.00	1.216
10.00	1,474	14.83	6.63	1.238
15.00	1,118	8.46	3.78	1.346
20.00	928.4	6.94	3.10	1.455
25.00	811.1	7.68	3.84	1.529
30.00	724.5	7.07	3.54	1.677
60.00	519.8	2.83	1.26	2.310
90.00	445.4	2.24	1.12	2.978
120.00	405.9	1.73	1.00	3.701

* $C_0 = .038 \times 10^{-3}$ mhos

$C_\infty = 3.36 \times 10^{-3}$ mhos

a in minutes

TABLE III

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0020 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT .2° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\Sigma d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.25	7,000	0.01[a]	0.01	1.016
0.43	5,000	0.01[a]	0.01	1.027
0.59	4,000	0.01[a]	0.01	1.036
1.00	2,710	101.00	45.09	1.059
2.00	1,620	14.87	6.64	1.112
3.00	1.184	10.91	4.87	1.162
4.00	961.2	6.93	3.09	1.211
5.00	822.7	7.75	3.46	1.258
6.00	727.9	8.00	3.57	1.303
7.00	658.0	6.98	3.12	1.358
8.00	604.1	4.80	2.14	1.394
9.00	561.8	5.50	2.46	1.437
10.00	525.9	4.94	2.21	1.483
15.00	418.7	3.74	1.67	1.700
20.00	362.0	3.00	1.34	1.932
25.00	326.3	3.24	1.45	2.131
30.00	302.3	2.45	1.09	2.345
60.00	239.2	1.72	0.77	3.668
90.00	217.7	1.39	0.70	5.004
120.00	206.7	1.74	0.78	6.376

* $C_0 = .052 \times 10^{-3}$ mhos

$C_\infty = 5.727 \times 10^{-3}$ mhos

a in minutes

TABLE IV

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT .2° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\Sigma d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.24	5,000	0.01[a]	0.01	1.022
0.34	4,000	0.01[a]	0.01	1.030
0.51	3,000	0.01[a]	0.01	1.043
1.00	1,806	11.75	5.88	1.080
2.00	1,083	8.06	4.03	1.148
3.00	809.0	5.83	2.91	1.212
4.00	665.7	5.22	2.61	1.273
5.00	575.6	1.05	0.53	1.332
6.00	512.7	2.23	1.11	1.390
7.00	466.6	2.24	1.12	1.448
8.00	419.3	19.10	9.55	1.527
9.00	402.9	1.86	0.93	1.562
10.00	380.1	0.89	0.45	1.617
15.00	308.5	1.00	0.50	1.894
20.00	270.9	0.63	0.32	2.168
25.00	247.6	0.48	0.24	2.441
30.00	231.2	0.55	0.27	2.723
60.00	189.2	0.32	0.16	4.445
90.00	174.7	0.00	0.00	6.254
120.00	167.4	0.17	0.08	8.130

* $C_0 = 0.055 \times 10^{-3}$ mhos

$C_\infty = 6.803 \times 10^{-3}$ mhos

a in minutes

TABLE V

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES:
.0010 MOLES OF 2,4-DINITROCHLOROBENZENE
IN CELL A AT 25° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.22	4,000	0.00[a]	0.00	1.045
0.34	3,000	0.02[a]	0.01	1.050
0.59	2,000	0.00[a]	0.01	1.084
1.46	1,000	0.01	0.00	1.198
3.00	606.7	0.69	0.31	1.387
4.00	507.2	0.79	0.35	1.506
5.00	446.0	0.97	0.43	1.622
6.00	404.3	0.58	0.26	1.737
7.00	373.9	0.85	0.38	1.850
10.00	317.4	0.85	0.38	2.189
12.00	294.3	0.33	0.15	2.420
15.00	271.3	0.03	0.01	2.754
17.00	261.1	0.74	0.33	1.958
20.00	248.3	0.78	0.34	3.306
23.00	239.1	0.69	0.31	3.633
25.00	233.9	0.66	0.30	3.863
30.00	224.1	0.51	0.23	4.425
60.00	199.5	0.92	0.41	7.736

* $C_\infty = 5.747 \times 10^{-3}$ mhos

$C_0 = 0.061 \times 10^{-3}$ mhos

a in minutes

TABLE VI

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0020 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT 25° C

Time in Minutes	Average R_t in ohms	$s = \sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.50	700.0	0.01[a]	0.01	1.165
0.64	600.2	0.01[a]	0.01	1.261
0.79	500.0	0.01[a]	0.01	1.259
1.15	400.0	0.03	0.01	1.349
1.41	350.0	0.02	0.01	1.422
1.81	300.0	0.07	0.03	1.533
3.00	230.1	5.43	2.43	1.838
4.00	202.7	3.91	1.75	2.077
5.00	184.6	3.53	1.58	2.327
6.00	171.9	2.18	0.98	2.584
7.00	160.0	1.98	0.89	2.930
10.00	146.6	1.13	0.51	3.573
12.00	139.1	0.41	0.18	4.146
15.00	132.4	0.48	0.22	4.956
17.00	128.4	1.30	0.58	5.662
20.00	125.5	0.47	0.21	6.334
23.00	122.9	0.44	0.20	7.172
25.00	121.4	0.42	0.18	7.772
30.00	118.6	0.39	0.17	9.073
60.00	111.5	0.42	0.18	19.759

* $C_\infty = 9.442 \times 10^{-3}$ mhos

$C_0 = 0.076 \times 10^{-3}$ mhos

a in minutes

TABLE VII

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT 25° C

Time in Minutes	Average R_t in ohms	$s = \sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.24	900.0	0.00[a]	0.00	1.100
0.41	600.0	0.01[a]	0.00	1.164
1.10	300.0	0.02[a]	0.01	1.406
3.00	171.8	1.23	0.61	2.042
4.00	152.4	1.05	0.52	2.359
5.00	140.0	0.71	0.36	2.687
6.00	132.1	0.61	0.30	2.993
7.00	126.2	0.56	0.28	3.304
10.00	115.2	0.24	0.12	4.250
12.00	110.9	0.14	0.07	4.870
15.00	106.6	0.41	0.21	5.779
20.00	104.4	0.26	0.13	6.434
20.00	101.9	0.03	0.02	7.434
23.00	100.2	0.55	0.27	8.357
25.00	99.3	0.17	0.09	8.956
30.00	97.5	0.07	0.03	10.514
60.00	92.5	0.07	0.03	21.825

* $C_0 = .085 \times 10^{-3}$ mhos

$C_\infty = 11.325 \times 10^{-3}$ mhos

a in minutes

TABLE VIII

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0010 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT 40° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_o}{C_\infty - C_t}$ *
0.41	1000	0.01[a]	0.01	1.145
0.56	800.0	0.01[a]	0.01	1.194
0.84	600.0	0.01[a]	0.01	1.280
1.00	536.2	1.14	0.51	1.326
1.50	413.5	1.99	0.99	1.476
2.00	348.3	2.02	0.91	1.626
2.50	309.3	1.70	0.76	1.769
3.00	282.0	1.11	0.50	1.917
3.50	262.5	1.87	0.84	2.060
4.00	247.6	1.45	0.65	2.203
4.50	235.4	0.69	0.31	2.354
5.00	225.6	0.91	0.41	2.503
6.00	212.1	0.95	0.43	2.774
7.00	201.6	0.62	0.28	3.062
10.00	183.2	0.76	0.34	3.878
15.00	168.2	0.67	0.30	5.246
20.00	160.4	0.77	0.34	6.235
30.00	152.2	0.44	0.20	9.583

* $C_o = .081 \times 10^{-3}$ mhos

$C_\infty = 7.326 \times 10^{-3}$ mhos

a in minutes

TABLE IX

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0020 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT 40° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.19	600.0	0.01[a]	0.01	1.666
0.24	500.0	0.01[a]	0.01	1.190
0.33	400.0	0.01[a]	0.01	1.253
0.52	300.0	0.01	0.01	1.374
1.00	204.1	2.28	1.02	1.678
1.50	165.9	1.57	0.70	1.996
2.00	146.0	1.35	0.61	2.316
2.50	133.6	0.94	0.42	2.644
3.00	125.5	1.08	0.48	2.963
3.50	120.7	1.25	0.56	3.218
4.00	115.2	1.03	0.46	3.603
4.50	111.7	1.15	0.52	3.927
5.00	109.1	1.00	0.45	4.225
6.00	105.0	0.98	0.44	4.841
7.00	101.9	1.04	0.46	5.491
10.00	96.3	0.75	0.34	7.460
15.00	91.9	0.67	0.30	10.846
20.00	89.2	0.85	0.38	15.504
30.00	86.9	0.85	0.38	25.322

* $C_0 = .10 \times 10^{-3}$ mhos

$C_\infty = 11.976 \times 10^{-3}$ mhos

a in minutes

TABLE X

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL A AT 40° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.23	400.0	0.02[a]	0.01	1.206
0.34	300.0	0.02[a]	0.01	1.296
0.62	200.0	0.03[a]	0.01	1.538
1.00	154.5	6.07	2.72	1.834
1.50	125.9	1.07	0.48	2.272
2.00	111.5	1.04	0.47	2.726
2.50	103.3	1.03	0.47	3.165
3.00	98.2	0.95	0.43	3.571
3.50	94.2	1.07	0.48	4.013
4.00	91.1	1.10	0.49	4.476
4.50	89.0	1.11	0.50	4.880
5.00	87.2	0.58	0.26	5.309
6.00	84.7	0.62	0.28	6.092
7.00	82.6	0.77	0.35	7.007
10.00	78.9	0.56	0.25	9.790
15.00	75.7	0.33	0.15	15.660
20.00	74.2	0.14	0.06	22.329
30.00	72.7	0.17	0.08	40.115

* $C_0 = 0.106 \times 10^{-3}$ mhos

$C_\infty = 14.104 \times 10^{-3}$ mhos

a in minutes

TABLE XI

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES : .0010 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 0.2° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.76	150,000	.02	.01	0.933
2.00	86,140	3,087	1,543	1.032
3.00	65,990	1,789	894	1.043
4.00	53,700	1,109	554	1.061
5.00	46,150	556.8	278.4	1.078
6.00	40,360	494.4	234.7	1.095
7.00	35,970	574.4	287.2	1.112
8.00	32,530	59.08	29.54	1.146
9.00	29,800	74.30	37.15	1.163
10.00	27,670	54.13	27.07	1.179
15.00	20,710	32.71	16.36	1.260
20.00	16,950	38.86	19.43	1.342
25.00	16,630	34.64	17.32	1.351
30.00	13,080	63.80	31.90	1.500
60.00	8,858	49.70	24.85	1.990
90.00	7,382	22.63	11.31	2.497
120.00	6,873	24.94	12.47	1.817

* $C_0 = .025 \times 10^{-4}$ mhos

$C_\infty = 2.242 \times 10^{-4}$ mhos

a in minutes

TABLE XII

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0020 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 0.2° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.36	100,000	0.02[a]	0.01	1.017
0.52	80,000	0.02[a]	0.01	1.024
0.63	70,000	0.01[a]	0.01	1.029
1.00	51,320	793.7	354.3	1.042
2.00	30,470	277.8	124.0	1.081
3.00	22,500	138.6	61.87	1.116
4.00	18,140	147.0	65.62	1.151
5.00	15,350	133.4	59.55	1.186
6.00	13,460	98.74	44.08	1.219
7.00	12,120	19.75	9.87	1.251
8.00	11,050	19.24	9.62	1.283
9.00	10,170	30.92	15.46	1.317
10.00	9,489	27.80	13.90	
15.00	3,372	11.70	5.85	1.504
20.00	6,239	14.59	7.30	1.659
25.00	5,540	11.18	5.59	1.815
30.00	5,062	12.00	6.00	1.968
60.00	3,794	10.10	5.05	2.932
90.00	3,377	10.10	5.05	3.868
120.00	3,151	9.43	4.72	4.881

* $C_0 = .033 \times 10^{-4}$ mhos

$C_\infty = 3.982 \times 10^{-4}$ mhos

a in minutes

TABLE XIII

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 0.2° C

Time in Minutes	Average R_t in ohms	$s = \sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.38	70,000	0.01[a]	0.01	1.023
0.49	60,000	0.01[a]	0.01	1.028
0.63	50,000	0.01[a]	0.01	1.036
1.00	36,230	432.1	216.17	1.054
2.00	21,160	98.34	49.17	1.103
3.00	15,590	45.06	22.53	1.158
4.00	12,680	61.40	30.70	1.192
5.00	10,800	68.34	34.17	1.235
6.00	9,521	14.32	5.68	1.277
7.00	8,588	20.98	10.49	1.319
8.00	7,867	11.36	5.68	1.360
9.00	7,297	5.20	2.60	1.400
10.00	6,836	15.68	7.84	1.440
15.00	5,384	7.68	3.84	1.641
20.00	4,619	4.12	2.06	1.840
25.00	4,164	8.54	4.17	2.039
30.00	3,831	1.45	1.23	2.234
60.00	2,999	2.24	1.12	3.423
90.00	2,696	8.12	4.06	4.726
120.00	2,537	4.00	2.00	6.182

* $C_0 = .039 \times 10^{-4}$ mhos

$C_\infty = 4.694 \times 10^{-4}$ mhos

a in minutes

TABLE XIV

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES : .0010 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 25° C

Time in Minutes	Average R_t in ohms	$s = \sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.55	40,000	0.00[a]	0.00	1.053
1.02	25,000	0.00[a]	0.00	1.097
1.35	20,000	0.00[a]	0.00	1.145
3.00	11,130	64.03	32.01	1.273
4.00	9,176	76.35	38.17	1.375
5.00	7.884	21.63	10.81	1.465
6.00	7.036	30.63	15.31	1.532
7.00	6,439	29.15	14.57	1.615
10.00	5,322	34.35	17.17	1.863
12.00	4,875	24.66	12.33	2.029
15.00	4,427	17.78	8.89	2.271
17.00	4,214	13.71	6.85	2.433
20.00	3,954	13.96	6.98	2.692
23.00	3,774	13.64	6.82	2.932
25.00	3,644	41.35	20.67	3.155
30.00	3,503	16.25	8.12	3.460
60.00	2,984	14.21	7.10	6.139

* $C_0 = .052 \times 10^{-4}$ mhos

$C_\infty = 3.993 \times 10^{-4}$ mhos

a in minutes

TABLE XV

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0020 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 25° C

Time in Minutes	Average Rt in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$
0.31	20,000	0.00[a]	0.00	1.070
0.73	10,000	0.01[a]	0.01	1.161
1.16	7,000	0.01[a]	0.01	1.251
3.00	3,810	35.50	17.75	1.601
4.00	3,265	19.16	9.58	1.783
5.00	2,920	12.53	6.26	1.968
6.00	2,689	14.66	7.33	2.149
7.00	2,521	15.94	7.97	2.330
10.00	2,215	6.08	3.04	2.863
12.00	2,091	7.00	3.50	3.224
15.00	1,966	2.65	1.32	3.761
17.00	1,905	3.17	1.59	4.130
20.00	1,838	3.74	1.87	4.667
23.00	1,786	3.32	1.66	5.233
25.00	1,757	2.24	1.12	5.628
30.00	1,705	2.65	1.32	6.565
60.00	1,577	3.32	1.66	12.056

* $C_0 = 0.050 \times 10^{-4}$ mhos

* $C_\infty = 6.910 \times 10^{-4}$ mhos

a in minutes

TABLE XVI

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 25° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\Sigma d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.49	10,000	0.01[a]	0.01	1.136
0.78	7,000	0.00[a]	0.00	1.212
1.25	5,000	0.01[a]	0.01	1.329
3.00	2,934	12.81	6.40	1.747
4.00	2,541	15.43	7.71	1.980
5.00	2,301	8.25	4.13	2.208
6.00	2,137	6.48	3.24	2.438
7.00	2,019	6.08	3.04	2.664
10.00	1,801	5.10	2.55	3.347
15.00	1,625	4.12	2.06	4.504
12.00	1,714	5.10	2.55	3.806
17.00	1,582	4.47	2.23	4.986
20.00	1,534	4.12	2.06	5.701
23.00	1,499	3.00	1.50	6.415
25.00	1,479	2.83	1.41	6.926
30.00	1,440	2.83	1.41	9.237
60.00	1,345	2.45	1.22	17.103

* $C_0 = 0.059 \times 10^{-4}$ mhos

$C_\infty = 7.842 \times 10^{-4}$ mhos

a in minutes

TABLE XVII

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0010 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 40° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.43	18,000	0.01[a]	0.01	1.111
0.54	15,000	0.01[a]	0.01	1.139
0.73	12,000	0.01[a]	0.01	1.184
1.00	9,618	28.53	14.27	1.275
1.50	7,280	23.17	10.34	1.355
2.00	6,076	24.82	11.08	1.462
2.50	5,313	11.92	5.32	1.570
3.00	4,795	18.30	8.17	1.676
3.50	4,425	16.88	8.44	1.779
4.00	4,129	12.53	6.27	1.886
4.50	3,903	11.05	4.93	1.991
5.00	3,718	18.30	8.17	2.096
6.00	3,443	7.68	3.43	2.302
7.00	3,239	8.60	3.84	2.512
10.00	2,860	8.66	3.87	3.154
15.00	2,564	8.31	3.71	4.219
20.00	2,419	6.24	2.78	5.240
30.00	2,260	0.71	0.03	7.554

* $C_0 = 0.050 \times 10^{-4}$ mhos

$C_\infty = 5.096 \times 10^{-4}$ mhos

a in minutes

TABLE XVIII

AVERAGE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0020 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 40° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.29	8,000	0.01[a]	0.00	1.1664
0.44	6,000	0.02[a]	0.01	1.235
0.58	5,000	0.01[a]	0.00	1.298
1.00	3,489	43.59	19.46	1.497
1.50	2,765	26.21	11.70	1.727
2.00	2,378	14.76	6.59	1.919
2.50	2,156	9.38	4.69	2.196
3.00	1,997	14.56	6.50	2.414
3.50	1,880	10.82	4.83	2.651
4.00	1,798	11.31	5.05	2.869
4.50	1,727	8.54	3.81	3.111
5.00	1,676	8.66	3.87	3.327
6.00	1,595	8.43	3.76	3.778
7.00	1,537	4.90	2.19	4.227
10.00	1,429	7.48	3.34	5.390
15.00	1,343	3.32	1.48	7.986
20.00	1,297	2.83	1.26	10.644
30.00	1,252	1.41	0.63	16.358

* $C_0 = 0.062 \times 10^{-4}$ mhos

$C_\infty = 8.503 \times 10^{-4}$ mhos

a in minutes

TABLE XIX

AVERATE RESISTANCES AND CONDUCTIVITY RATIOS AT GIVEN TIMES: .0025 MOLES OF 2,4-DINITROCHLOROBENZENE IN CELL B AT 40° C

Time in Minutes	Average R_t in ohms	$s=\sqrt{\frac{\sum d^2}{N-1}}$	$\frac{s}{\sqrt{N}}$	$\frac{C_\infty - C_0}{C_\infty - C_t}$ *
0.26	6,000	0.00[a]	0.00	1.191
0.47	4,000	0.00[a]	0.00	1.323
0.75	3,000	0.00[a]	0.00	1.488
1.00	2,549	13.04	7.54	1.633
1.50	2,079	44.61	25.79	1.912
2.00	1,744	40.99	23.69	2.326
2.50	1,641	3.16	1.83	2.540
3.00	1,539	4.12	2.38	2.833
3.50	1,462	4.12	2.38	3.139
4.00	1,403	4.47	2.58	3.454
4.50	1,361	3.61	2.09	3.740
5.00	1,324	2.45	1.42	4.054
6.00	1,271	2.22	1.28	4.652
7.00	1,231	2.24	1.28	5.287
10.00	1,162	2.00	1.16	7.113
15.00	1,105	3.16	1.83	10.434
20.00	1,075	1.73	1.00	12.435
30.00	1,046	1.73	1.00	22.552

* $C_0 = 0.077 \times 10^{-4}$ mhos

$C_\infty = 10.000 \times 10^{-4}$ mhos

a in minutes

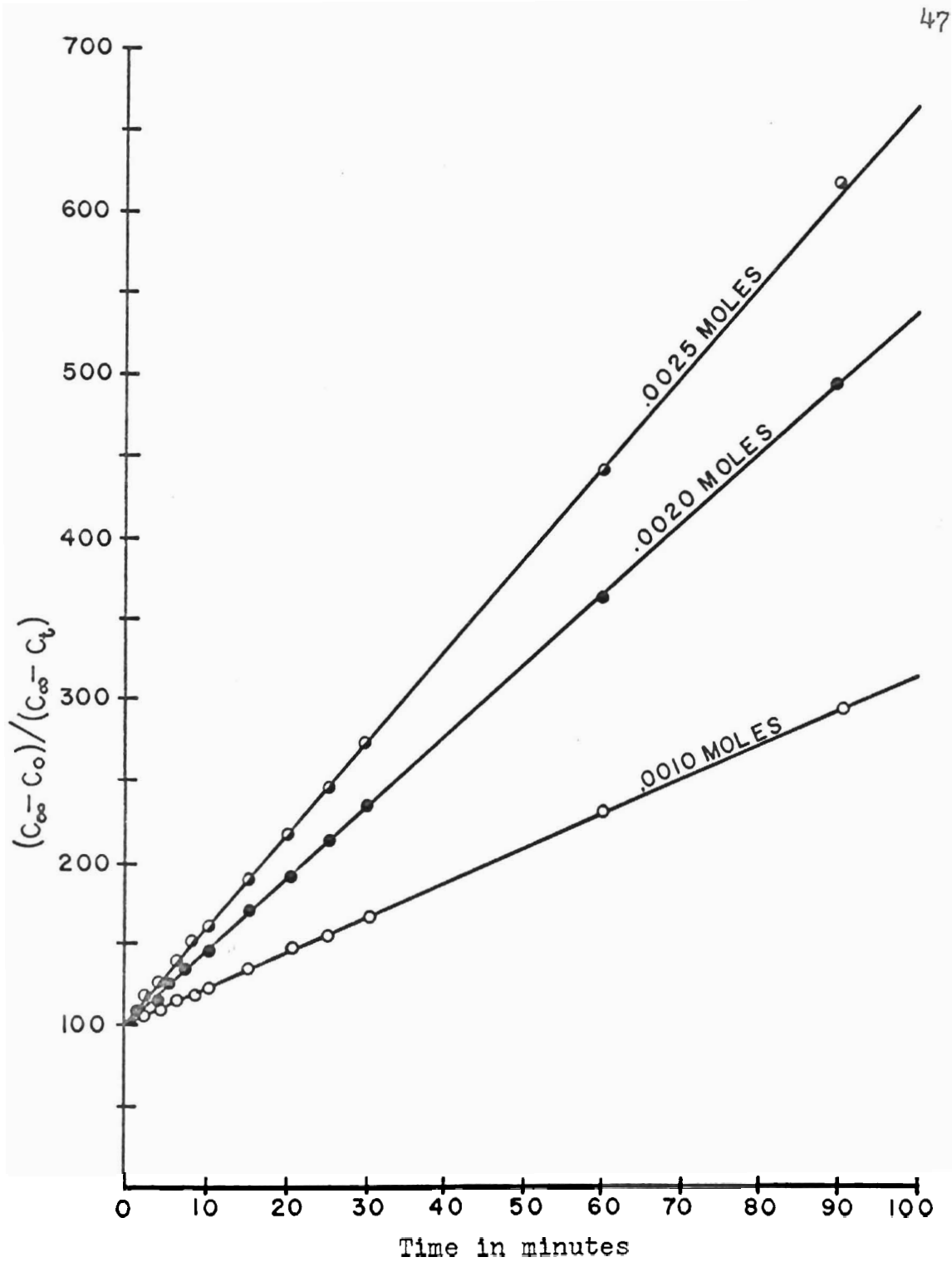

Figure 2. Increase in conductance ratio with time: cell A at 0.2° centigrade.

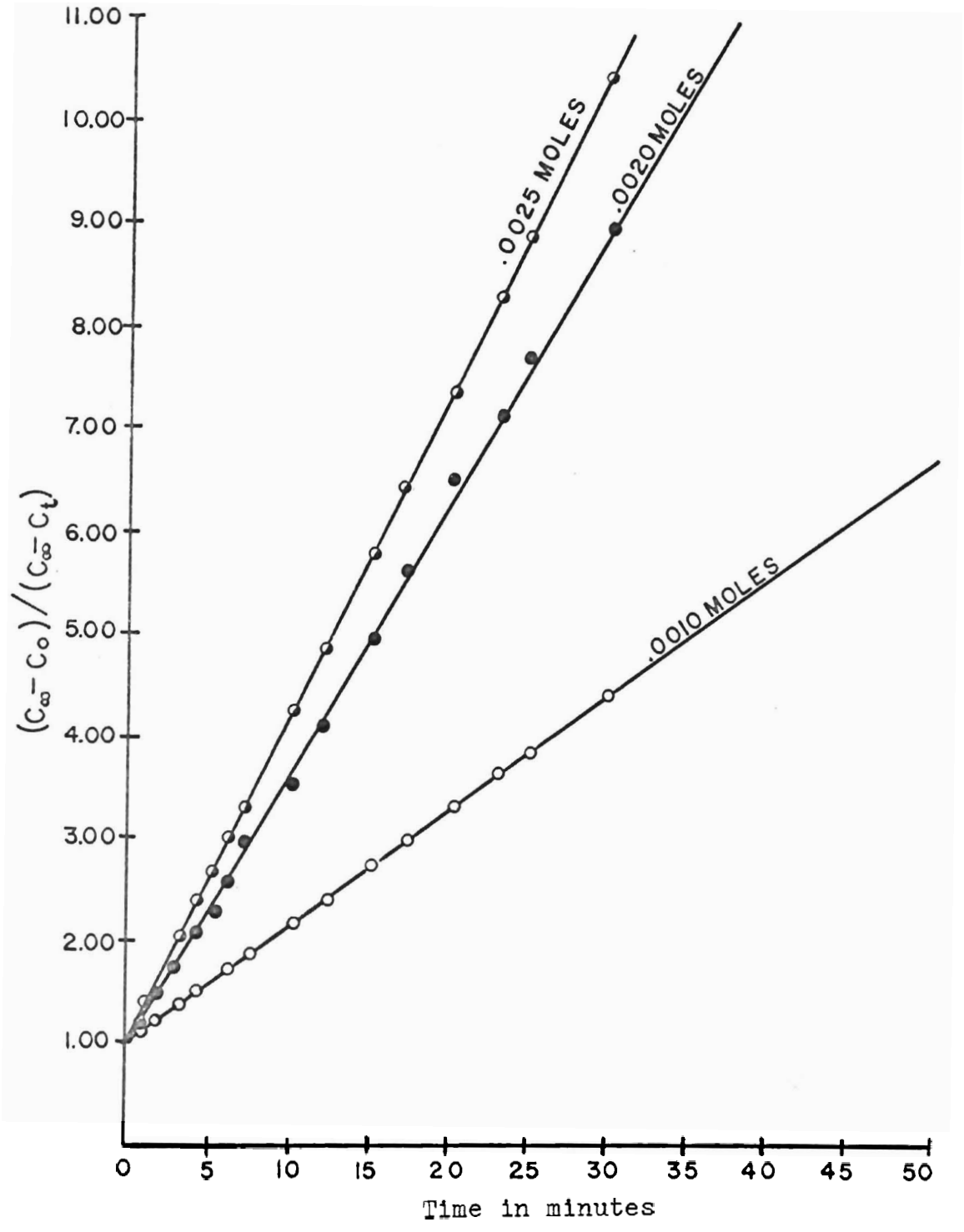

Figure 3. Increase in conductance ratio with time: cell A at 25° centigrade.

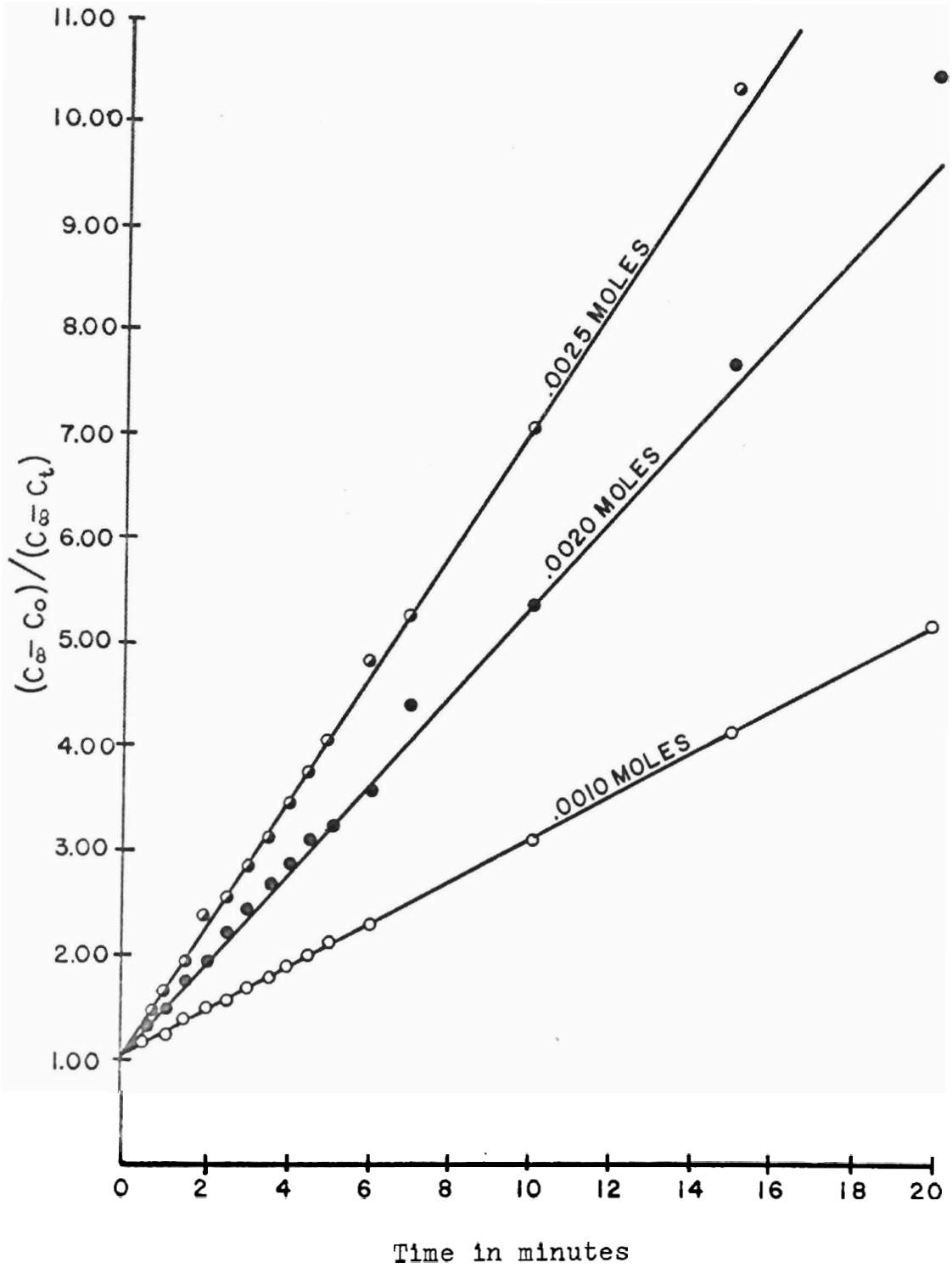

Figure 4. Increase in conductance ratio with time: cell A at 40° centigrade.

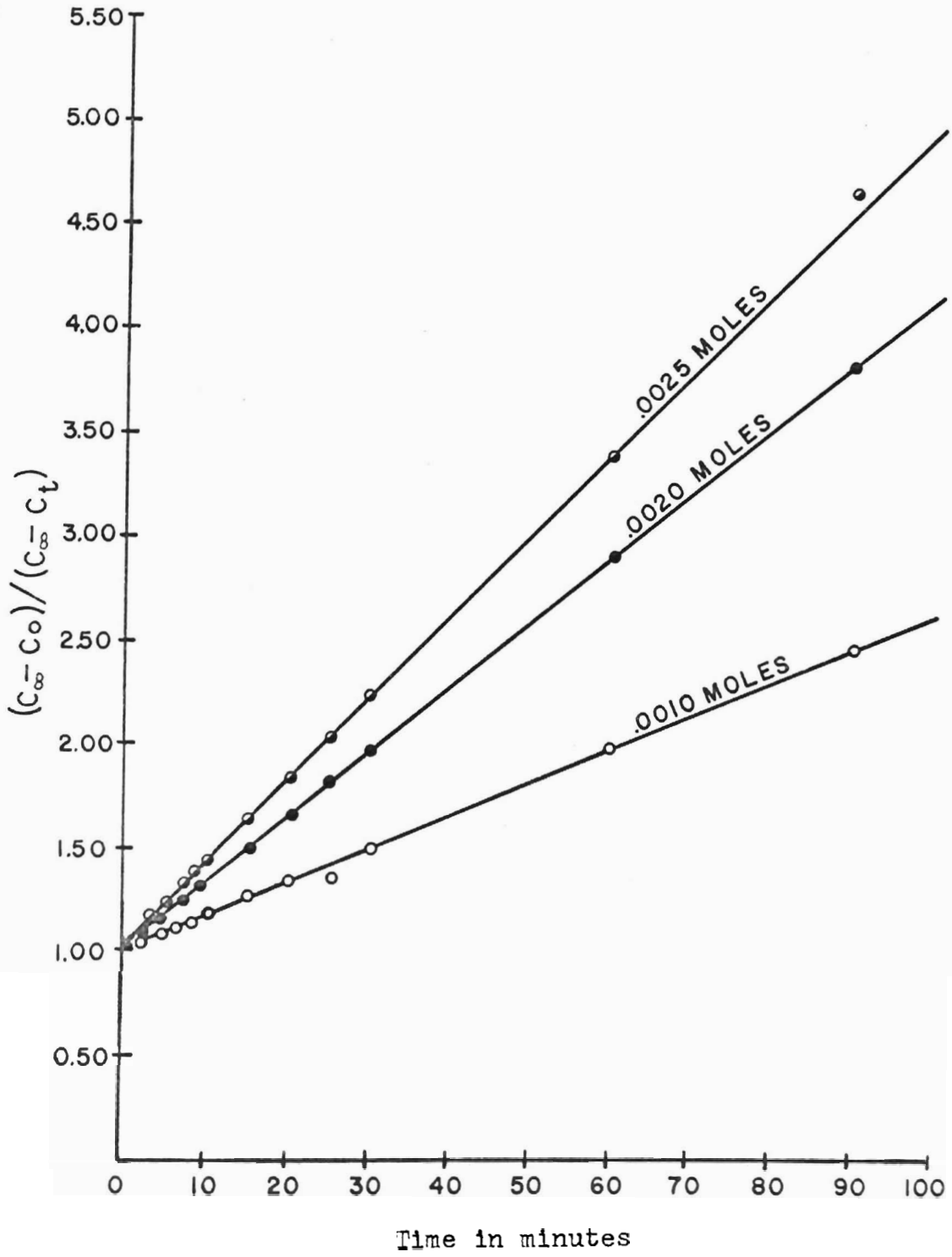

Figure 5. Increase in conductance ratio with time: cell B at 0.2° centigrade.

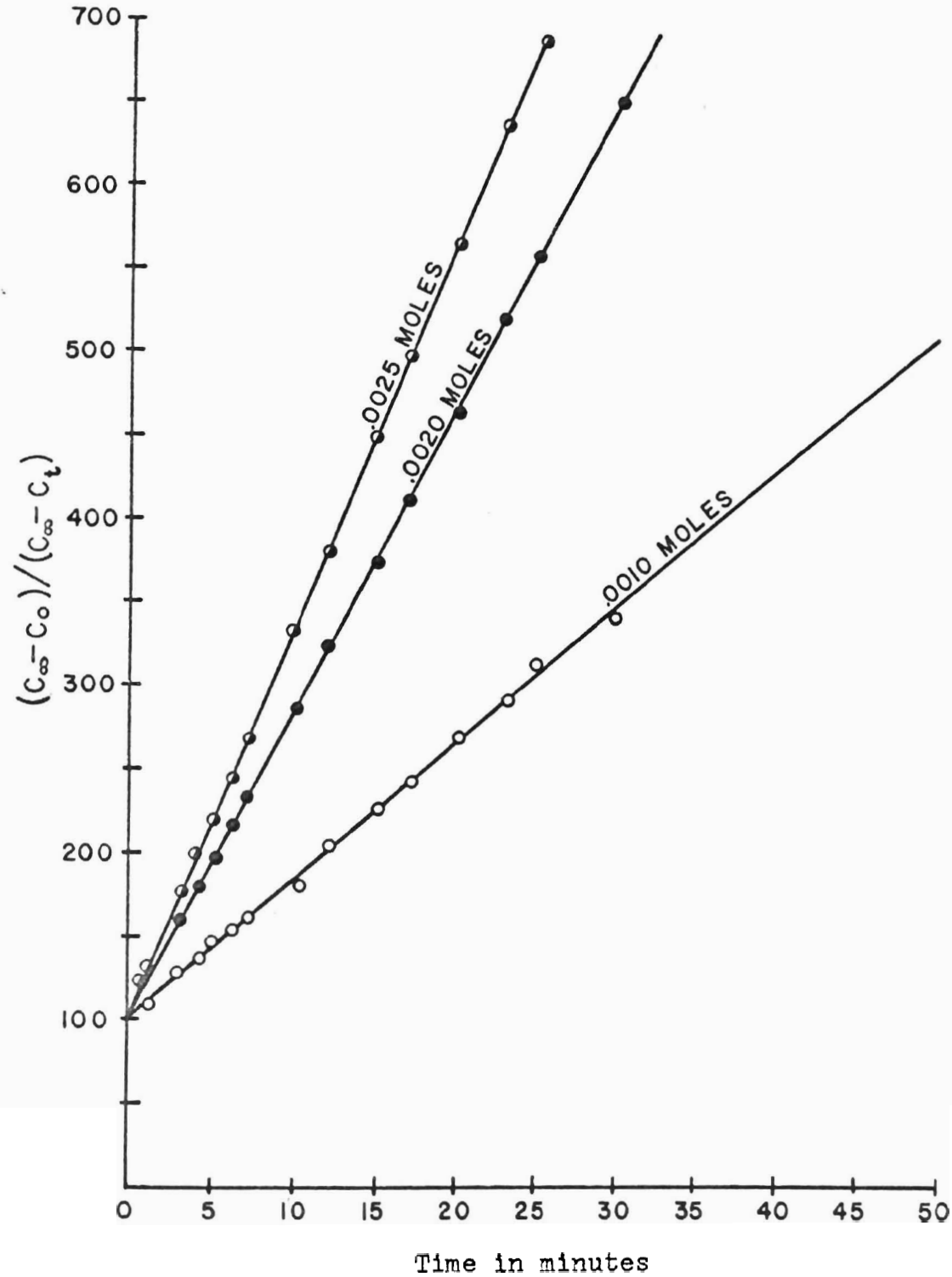

Figure 6. Increase in conductance ratio with time: cell B at 25° centigrade.

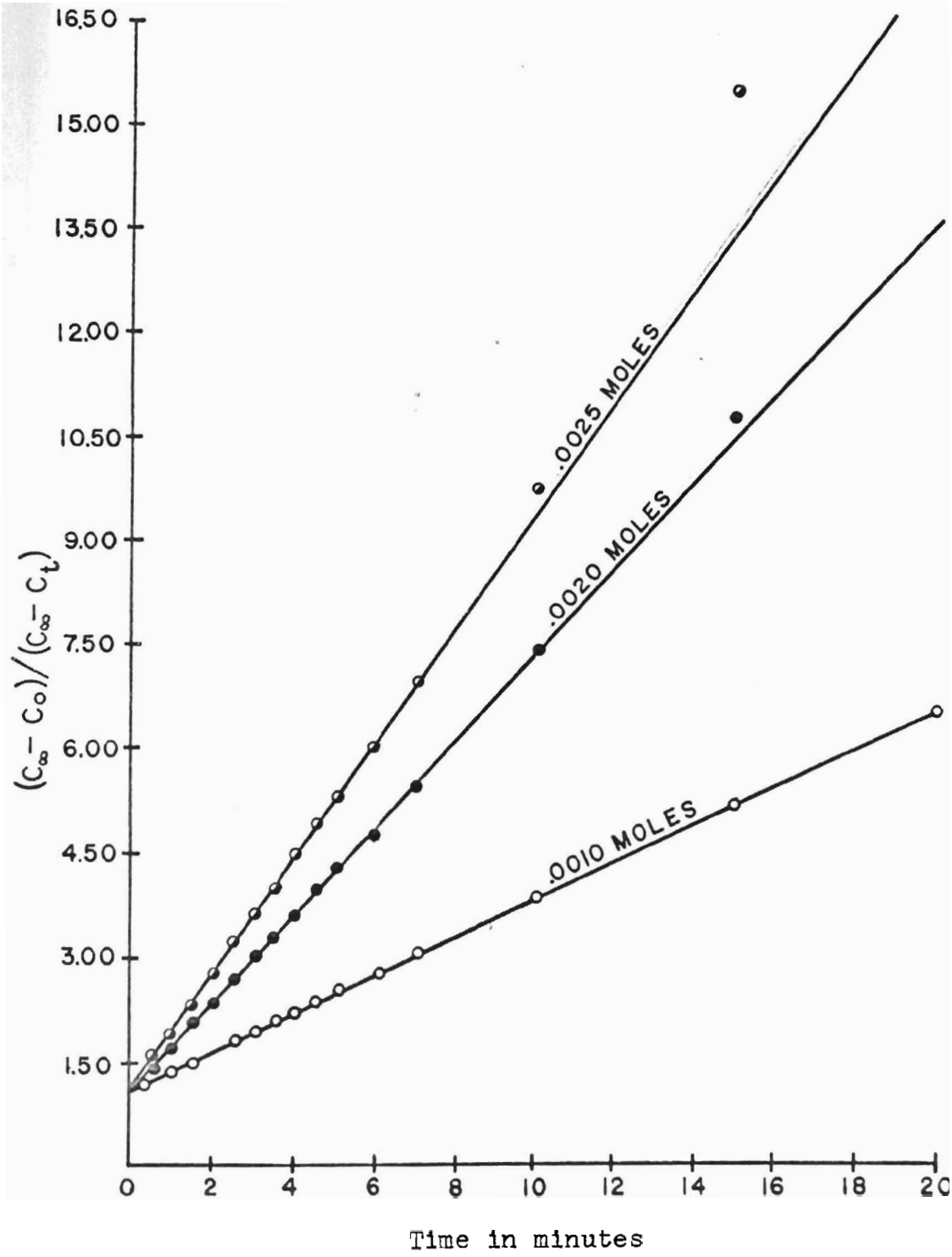

Figure 7. Increase in conductance ratio with time: cell B at 40° centigrade.

CHAPTER IV

CONCLUSIONS AND DISCUSSION

Finding the reproducibility of the data was a necessary preliminary procedure. The values obtained indicated the maximum precision which could be expected from cells A and B at different cell resistances. Table XX

TABLE XX

REPRODUCIBILITY OF CELL A AND CELL B AT VARIOUS KCl CONCENTRATIONS AT 25° C

KCl concentration in moles per liter	Cell A		Cell B	
	Cell Constant in cm^{-1}	Resistance of cell in ohms	Cell Constant in cm^{-1}	Resistance of cell in ohms
.001	.1237±.0008	838.0	- - -	- - -
.005	.1246±.0005	173.0	1.4350±.0011	2000
.01	.1250±.0002	88.5	1.4368±.0007	1017

showed that the least deviation occurred when the cell resistance was lowest. The range of values expected was four times greater at .001 moles per liter than at .01 moles per liter. Also, cell B's deviations were larger than Cell A's deviations. The deviations were rather misleading, however, because the relative per cent deviation was

actually less in cell B and at 838 ohms than at 88 ohms in cell A. The equipment was considered precise enough.

Tables II through XIX contain the following five columns: (1) time elapsed from start of reaction, (2) average resistances at time t, (3) standard deviation of an individual reading, (4) standard deviation of the mean, and (5) calculated conductivity ratio at time t. The average resistances were obtained from five trials but with only one of the trials actually being allowed to react completely.

The average resistances were lowest, or the conductances highest, when the highest concentrations of reactants were involved. This was expected because of the dependency of conductance on the number of ions present. The average resistances changed more rapidly at the start of the reaction than at the mid-point for example because of the greater production of ions. The average resistance range for cell A was 12,000 ohms for .001 moles of 2.4-dinitrochlorobenzene at 0.2° C to 72.7 ohms for .0025 moles of 2-4-dinitrochlorobenzene at 40° C. For cell B, the highest average resistance was 150,000 ohms for .001 moles of 2,4-dinitrochlorobenzene at 0.2° to 1,046 ohms for .0025 moles of 2,4-dinitrochlorobenzene at 40° C.

The standard deviation of an individual reading

signifies that sixty-eight per cent of one hundred readings would have values that were between the limiting values of two standard deviations. In both cells A and B, the standard deviation was less at .0025 moles than either .0020 moles or .0010 moles of 2,4-dinitrochlorobenzene, with .0020 moles being the largest. There is no explanation why .0020 moles should deviate the most.

The reaction temperature effected the precision of the readings. Forty degrees centigrade gave the least standard deviation and 0.2° C gave the greatest for cell B. Cell A at 40° C had the smallest standard deviations for concentrations of .0020 and .0025 moles 2,4-dinitrochlorobenzene but at 25° C, .0010 moles deviated the least. The least concentrated, .0010 moles, deviated the greatest at 0.2° C. These results were contrary to this experimenter's original idea that because the reaction proceeded more slowly at 0.2° C, the greater time available for obtaining a null-point would permit more precise measurements. The precision at 0.2° C was approximately one-tenth that at the other two temperatures.

The first three values in each table were measurements of the times necessary for the reaction to obtain predetermined resistances. Generally, the standard deviations were approximately one-hundredth of a minute or less. Many deviations were less than one-hundredth of a minute

but were recorded as such because of the inability to time the reaction more accurately.

Upon modifying the preset-resistance procedure, the standard deviation (now in ohms) was largest and progressively decreased until approximately one-half of the resistance measurements were determined. At which time, the standard deviations continued to decrease but decreased more gradually. The original large deviations were probably caused by the inaccuracy of the null-points, because of the rapidity of the reaction and the extremely high resistances. The slidewire dial could have had an uncertainty of two divisions in either direction of the true setting. Since the cell resistances were the products of the slidewire ratios and the corresponding decade box resistances, two divisions changed the resistances considerably. For example, if the decade box resistance was 120,000 ohms at a slidewire reading of 456 divisions the cell resistance was 117,900 ohms while at 458 divisions the cell resistance equalled 118,100 ohms. At the original high cell resistances, the accurate null-point was difficult to achieve because of the limitations of the cell designs. For cell B, resistances below 35,000 ohms gave moderately reproducible readings and below 2,500 ohms gave very reproducible resistances. For cell A, resistances below 250 ohms gave

excellent reproducibility. For both cells, the majority of the standard deviations were less than 0.3 per cent of the average resistances and approximately one-half the standard deviations of the individual readings were within the reproducibility of the equipment.

The standard deviations of the means were more precise than the standard deviation of an individual measurement by the square root of five. These values indicated that the mean of a series of trials would have a sixty-eight out of one hundred chance of being in the range imposed by plus and minus one deviation of the mean. The previous statements made in reference to the standard deviations of individual measurements applied to the standard deviations of the means.

The conductances for various times, t, were obtained from the reciprocals of the corresponding average resistances. The two constants, C_o and C_∞, were dependent upon the original concentrations and the reacting temperatures. The original conductances of the reacting solution at time zero (C_o) ranged from 3.8×10^{-5} mhos to 10.6×10^{-5} mhos for cell A with the lowest conductance being with the least concentrated solution and at 0.2° C. For cell B the range of C_o was 2.5×10^{-6} mhos to 7.7×10^{-6} mhos with the concentrations and temperatures being the same as in cell A. The final conductances of the reaction products, C_∞, ranged from

3.360×10^{-3} mhos to 14.10×10^{-3} mhos for cell A and 2.242×10^{-4} mhos to 10.00×10^{-4} mhos for cell B. Both extreme ranges were between the lowest concentrations and temperatures to the highest concentrations and temperatures. The increase in conductance was approximately one-hundred fold.

Since the conductances of the 2,4-dinitrochlorobenzene solutions were too low to be measured and those of the piperidine solutions were readily measurable, the original conductances were considered to be dependent upon the piperidine and not the 2,4-dinitrochlorobenzene or the 95 per cent ethanol.

The increases of the original and final conductances with concentration was to be expected because of the large increase in total ion concentrations.

The temperature effects upon the conductances of the same concentrations of substances, are shown in Table XXI. The ratios of the conductances at 40° C to 0.2° C are approximately two and the final conductances the ratios are slightly greater than two.

TABLE XXI

RATIO OF CONDUCTANCES AT 40° C TO 0.2° C

Concentration of piperidine in moles/liter	Cell A		Cell B	
	C_o/C_o	C_∞/C_∞	C_o/C_o	C_∞/C_∞
.20	2.00	2.28	2.11	4.19
.40	1.88	2.14	1.90	2.09
.50	2.00	2.14	1.94	1.73

This again was understandable because the hinderance to the movements of the ions is decreased with increasing temperature.

The temperature effect upon the accuracy of the ratio, $\frac{C_\infty - C_o}{C_\infty - C_t}$, would not be appreciable because all three values increased with temperature. Unfortunately, no means was available for determining the relationship of C_t at 0.2°C and the corresponding C_t at 40° C.

Figures 2 through 7 represent the plotting of the conductance ratio, $\frac{C_\infty - C_o}{C_\infty - C_t}$, versus time (t) in minutes for cells A and B containing various reactant concentrations at different temperatures. It was found that the best straight lines occurred when the original concentrations of 2,4-dinitrochlorobenzene were .0010 moles and least when the concentrations were .0020 moles. It is interesting

to note that while the largest deviations from the average resistances occurred at .0010 moles and at 0.2° C, these values represented a straight line best. The two points at 40° C which were far from the drawn line probably had their deviations increased by the mathematical characteristic of the ratio involved.

The straight lines obtained verified the simple linear function of conductance and concentrations as well as the credibility of the following mathematical expression relating the conductances to the specific rate constants:

$$\frac{C_{\infty} - C_{o}}{C_{\infty} - C_{t}} = 2kat + 1$$

The slopes and y-intercepts obtained from the method of least squares are given in Table XXII. As can be seen, the slopes increase with increasing concentrations as well as with increasing temperatures. This was expected because while C_t becomes increasingly larger, the difference $(C_{\infty} - C_t)$ became increasingly smaller.

TABLE XXII

SLOPES AND Y-INTERCEPTS OF CONDUCTANCE CURVES

Moles of 2,4-dinitrochlorobenzene in 29.5 ml of solution	Slope			y-intercept		
	0.2°C	25°C	40°C	0.2°C	25°C	40°C
			Cell A			
.0010	.0024	.1125	.1896	1.015	1.042	1.051
.0020	.0451	.2576	.6359	1.020	1.017	1.035
.0025	.0568	.3152	.8611	1.046	1.097	0.990
Concentration in moles/39ml			Cell B			
.0010	.0166	.0846	.2151	1.001	1.013	1.022
.0020	.0345	.1835	.4559	1.096	1.033	1.034
.0025	.0400	.2340	.6067	1.032	1.028	1.030

The y-intercepts were all close to one which further verifies the preceding expression.

The calculated specific rate constants are given in Table XXIII. The specific rate constants are theoretically independent of the concentration. The rate constants in Table XXIII do not vary with the original concentration of 2,4-dinitrochlorobenzene but they do vary with the temperature.

TABLE XXIII

SPECIFIC RATE CONSTANTS AND HALF-LIVES AT VARIOUS CONCENTRATIONS AND TEMPERATURES

Concentration of 2,4-dinitrochlorobenzene in moles/vol. of cell	k (liter mole^{-1} minute^{-1})			$t_{\frac{1}{2}}$ (minutes)		
	0.2° C	25° C	40° C	0.2° C	25° C	40° C
			Cell A			
.0010	0.3263	1.603	4.127	43.67	8.89	3.45
.0020	0.3212	1.834	4.526	22.17	3.88	1.57
.0025	0.3238	1.797	4.909	17.61	3.17	1.16
			Cell B			
.0010	.3229	1.650	4.195	60.38	11.81	4.65
.0020	.3064	1.754	4.049	40.38	5.45	2.19
.0025	.3122	1.825	4.732	24.98	4.27	1.65

The average rate constants for both cells at 0.2° C, 25° C, and 40° C were 0.3188, 1.744, and 4.423 liters mole^{-1} minute^{-1} respectively. The values obtained by Bunnett and Crockford[1] by volumetric titrations of the chloride ions were 0.195 and 1.11 liters mole^{-1} minute^{-1} for 0° C and 25.3° C respectively. The corresponding rate constants determined spectrophotometrically were 0.226 and 1.31 liters moles^{-1} minutes^{-1}. The specific rate constants determined conductometrically were larger than

[1] Bunnett and Crockford, op. cit., p. 553.

those obtained by Bunnett and Crockford. A small increase from the absolute value might have been due to the conductance of the piperidinium ion but this would be quite small. This experimenter used the average of six concentrations at each temperature while Bunnett used only one. It seems plausible that a continuous monitoring of the reaction progress without needing to remove an aliquot would be the most accurate.

The half-lives of the reactions, as shown in Table XXIII, are temperature and concentration dependent. The half-lives are inversely proportional to the concentration of the reactants. The half-lives decrease as the temperature increases.

The plotting of the logarithm of the specific rate constants versus the reciprocal of the absolute temperature gave a straight line as shown in figure 8. Since three plotted points fall on the straight line, the accuracy of the specific rate constants are further substantiated.

The slope of the straight line in figure 8 equalled -2.313×10^{3} and the activation energy E, was 10.66 Kcal. The activation energy obtained by using the integrated Arrhenius equation was 10.58 Kcal. This activation energy represents the energy the 2,4-dinitrochlorobenzene and piperidine molecules must acquire in order to undergo reaction. The activation energy in other solvents (50%,

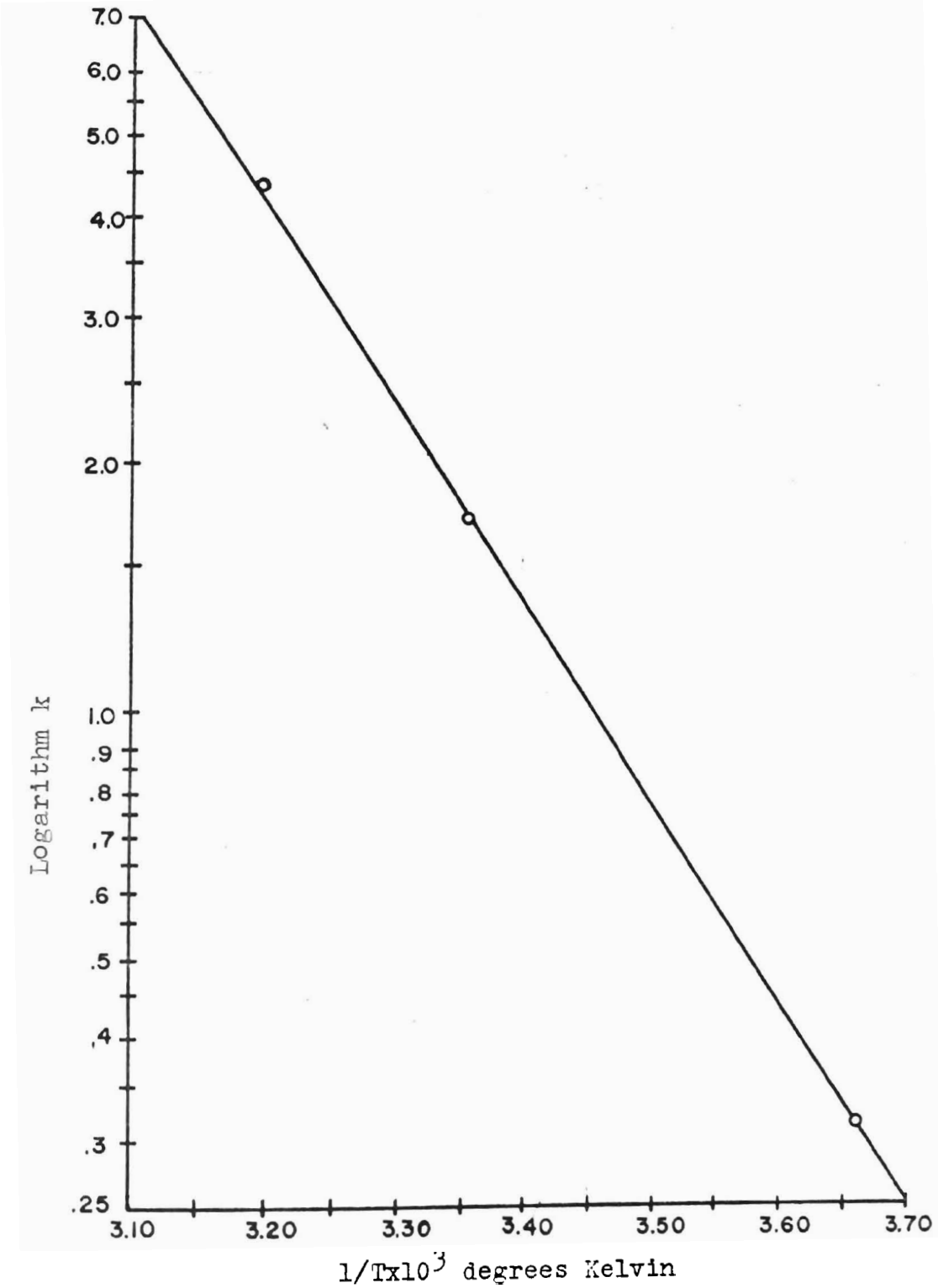

Figure 8. Variation of logarithm k with the reciprocal of absolute temperature.

60%, 75% dioxane) are nearly the same as in 95 per cent ethanol.[1]

The change in entropy of the system was -21.84 cal. deg^{-1} $mole^{-1}$. This value gives an indication of the reaction. A reaction which has a large decrease in entropy indicates the formation of an activated state.

The conductrometric analysis of the reaction of 2,4-dinitrochlorobenzene with piperidine in 95 per cent ethanol was feasible. The apparatus could have been improved by the use of a more constant water bath. The temperature variable was plus or minus .1° C in some instances which was too large.

Also, another method of introducing the piperidine into the cell would be advantageous. A modification of the Folin-Wu tube might prove useful because the reactants could be mixed instantaneously without either leaving the water bath.

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[1] J. F. Bunnett and R. J. Morath, "The Rates of Condensation of Piperidine with 1-chloro-2,4-dinitrobenzene in Various Solvents", Journal of the American Chemical Society, LXVII (1955), 5165.

CHAPTER V

SUMMARY

A conductometric method for determining the reaction kinetics of 2,4-dinitrochlorobenzene with piperidine in 95 per cent ethanol was satisfactory. The absolute error was large at the beginning of the reaction, because of the magnitude of the resistances measured. The corresponding relative errors were generally less than 0.4 per cent for an individual measurement and 0.2 per cent for the deviation of the mean. The absolute error decreased with the progress of the reaction but the relative error remained constant.

When the conductance ratios for the three concentrations at one temperature were plotted against the time of reaction, three straight lines were formed which radiated from a nearly constant y-intercept. The fact that straight lines were formed verified the equations relating the conductances with the specific rate constants. The close proximity of points to the lines gave another indication of the accuracy of the method.

The average specific rate constant for the two cells were 0.3188, 1.744 and 4.423 liters $mole^{-1}$ $minute^{-1}$ at 0.2°C, 25°C, and 40°C respectively. These values were higher than Bunnett and Crockford's[1] which were 0.195 and 1.11 liters

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[1] Bunnett and Crockford, op. cit., p. 555.

mole^{-1} minute^{-1} for 0°C and 25.3°C respectively.

The change of the specific rate constants with temperature was shown in Figure 8 to be linear. The activation energy was calculated from the slope of this straight line was 10.66 K. calories. The activation energy calculated from the integrated Arrhenius equation was 10.58 K. calories. The change in entropy for this reaction was -21.84 calories degree^{-1} mole^{-1}.

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